Indian J. Phys. **77B** (6), 651-655 (2003)

AN INTERNATIONAL JOURNAL
IJP B

Dielectric relaxation study of intramolecular hydrogen bonded o-hydroxy acetophenone in non-polar solvents

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Received 21 July 2003, accepted 28 August 2003

Abstract . The static permittivity of o-hydroxy acetophenone (OHA) in three non-polar solvents namely benzene, 1,4-dioxane and cyclohexane have been measured at 303K and frequency 100 KHz. The data were used to evaluate Kirkwood correlation factor g, excess molar polarization (Δp), excess correlation factor (δg) and excess free energy (ΔG) It is observed that in dilute solutions, β- multimers with antiparallel dipolar orientation predominate for benzene and cyclohexane but in 1,4-dioxane α- multimers with parallel orientation dominate in the entire concentration range. OHA behaves as a rigid molecule because of the intramolecular hydrogen bond between hydrogen and acetyl groups

Keywords Dielectric constant, Kirkwood correlation factor, excess molar polarization, excess free energy

PACS Nos. 77.22 Ej, 31.70 Dk, 51 30.+i

1. Introduction

Many workers [1-6] have done extensive work on dielectric behaviour of acetophenone and its derivatives which provides structural information along with its interaction with non-polar solvents. Authors [7] have already reported the dielectric relaxation study of acetophenone, pyridine and their binary mixtures in dilute solutions of benzene. Recently Messieh [8] reported the effect of solvent viscosity on the dielectric relaxation of some acetophenone derivatives. Acetophenone possesses intermediate character between aromatic and aliphatic compounds. It is also a non-hydrogen bonded liquid and behaves as a rigid polar molecule [1]. If it is treated as a benzene derivative, a large acetyl group ($-CO-CH_3$) could significantly hinder the molecular association. Its o-hydroxy derivative namely o-hydroxyacetophenone (OHA) is classified as having a strong intramolecular hydrogen bond [6] of type -OH--O-C and may be looked upon as a rigid molecule for dielectric absorption. Therefore, it is of great interest to study the dielectric behaviour of OHA with non-polar solvents to understand the role of hydrogen bonding in molecular interactions taking place in the system

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Earlier, we reported [9] the dielectric response of cyclohexylamine (CHA) in different non-polar solvent. The measured values of dielectric permittivity were used to compute Kirkwood correlation factor (g), molar polarization (P_2), excess correlation factor (δg) and excess free energy (ΔG). The presence of α- and β- multimers was identified for the different environments.

Attempts have been made by researchers [7-10] to study the dielectric properties of binary mixtures. In all these cases only the long-range dipolar interaction between the molecules are taken into consideration. Winkelmann and Quitzsch [11], however, developed a comprehensive relation linking the dielectric constant of a binary mixture with those of the pure components considering both long range and short range dipolar interaction between the like as well as unlike molecules. Besides the Kirkwood-Fröhlich linear correlation factor of dielectric polarization g, which is a measure of short range intermolecular force [12] leading to dipole-dipole interaction in the like molecules, they introduced the concept of mutual correlation factor for unlike molecules to account for the short range dipole-dipole interaction between them.

In this paper, an attempt has been made to study the inter- and intramolecular hydrogen bonding and formation of multimers to understand the molecular behaviour of OHA in benzene, 1,4-dioxane and cyclohexane environment by evaluating various dielectric parameters *i.e.* Kirkwood correlation factor (g), excess molar polarization (Δp), excess correlation factor (δg) and excess free energy (ΔG).

2. Method of measurement and analysis of data

OHA (AR grade) from Sisco Research Laboratory (SRL), benzene, 1,4-dioxane and cyclohexane, all AR grade were procured from BDH (British Drug House, E. Merk Limited, Bombay), India. Benzene, 1,4-dioxane and cyclohexane were distilled twice before use.

The experimental set-up, procedure and principle involved in determining static permittivity (ϵ_0), the optical permittivity (ϵ_∞) are the same as described earlier by the authors [7,9]. All measurements were made at constant temperature 303K.

Kirkwood correlation factor (g) has been calculated by using the modified Kirkwood-Fröhlich [13] equation for the binary mixture. The molar polarization [14] of binary mixture is given by

$$P_m = \frac{3V_1 f_1(\epsilon_1 - 1)}{\epsilon_m + 2} \cdot \frac{1}{2\epsilon_m + \epsilon_1} + \frac{3V_2 f_2(\epsilon_\infty - 1)}{2\epsilon_m + \epsilon_\infty}$$

$$+ g' \frac{4\pi N \mu^2 f_2(\epsilon_\infty + 1)^2 (2\epsilon_m + 1)}{9KT(2\epsilon_m + \epsilon_\infty)^2} \qquad (1)$$

Here, ϵ_m is the static dielectric constant of the solution, ϵ_∞ is the square of refractive index at the frequency of D-lines of sodium for pure solute, ϵ_1 is the static dielectric constant of pure solvent, f_1 is the mole fraction of the solvent, f_2 is the mole fraction of the solute, V is the molar volume of the solution and V_1 and V_2 are the molar volume of pure solvent and pure solute respectively. K, T and N are Boltzmann's constant, absolute temperature and Avogadro's number, respectively. g' is the Kirkwood-Fröhlich linear correlation factor for the pure polar solute.

The excess molar polarization in the binary mixture is given by

$$\Delta P = P_m - (f_1 P_1 + f_2 P_2), \qquad (2)$$

where P_1 and P_2 are the molar polarization of non-polar and polar liquids respectively.

The excess Gibb's free energy of mixing (ΔG_I) in the binary mixture was obtained by the expression used by Swain and Roy [15]. Davis and Douheret [16] developed a mixture equation purely from empirical considerations and introduced a parameter called excess correlation factor (δg) to represent the departure from ideality. Ray and Roy [17] also give the expression for excess free energy of mixing (ΔG_{II}) for the binary mixture of polar and non-polar solvents using excess correlation factor δg in place of g.

3. Results and discussion

The dielectric constant of OHA with non-polar solvents viz benzene, 1,4-dioxane and cyclohexane has been determined at

Table 1. Values of ϵ_0, g, ΔP, δg, ΔG_I and ΔG_{II} with concentration in different solvents at 313K

Mole fraction of OHA	ϵ_0	g	ΔP (cc)	δg	ΔG_I (J/mole)	ΔG_{II} (J/mole)
Solvent: Benzene						
0	2.264	0	0	0	0	0
0.07505	2 825	0.78	2 09	-0.26	197 23	171 30
0 14456	3 480	0.84	4 23	-0.24	324 00	246 13
0 22035	4.450	0.96	7.06	-0 15	395 97	262 39
0.30343	6 670	1.35	13 46	0.18	338 53	217 36
0 36776	9.600	1.80	18 36	0.60	224 87	159 08
0.46445	12 625	2 03	18.32	0.77	142 99	101 09
0 54251	14.175	2 02	16.04	0 72	105 90	68 69
0 64650	15 175	1.88	11 45	0 52	86 46	43 76
0 75491	15.675	1 72	6 04	0 30	80.24	26 45
0.85557	16 100	1 60	0 97	0.12	70 63	12 02
Solvent: 1,4-Dioxane						
0	2 201	0	0	0	0	0
0.08528	4.320	2 27	14 91	1.23	147 72	143 70
0 13829	5 320	2.01	17.33	0 93	192 81	177 28
0.20635	6.250	1.74	17.36	0.62	240.81	199 05
0.28009	8.550	1.97	20 43	0.81	206 11	168 89
0.35775	10.900	2.11	21 01	0.91	162.29	131 04
0 44408	13 250	2.19	19.79	0.94	112.93	88 07
0 54335	16 000	2.28	17 49	0.97	42.61	32 18
0.62851	16.175	2.05	13.26	0 69	44 66	26 64
0 74970	16.350	1 80	6 75	0 38	48.03	18 07
0 86715	16.375	1.61	0 48	0.13	56.77	9 26
Solvent: Cyclohexane						
0	2 201	0	0	0	0	0
0.10372	2.375	0 21	-4.32	-0.85	321.04	245 14
0.17668	2.650	0.32	-4.98	-0.78	518 02	323.04
0.26019	3.650	0.67	2 14	-0.47	589.32	316 99
0 35062	4.925	0.88	6.99	-0.31	596.57	269 65
0.44145	9.050	1.64	19.40	0.39	314.64	184.12
0 52518	12.235	1.96	20.66	0.67	184.57	117 81
0.61327	13.120	1.83	15.99	0.48	174.59	88 56
0 70742	14.175	1.73	10.98	0.33	147.89	56 00
0.81169	15.075	1.62	4.92	0.17	121.68	27 01
0.90419	16.175	1.58	-0.22	0.07	71.61	7 62
1	17.490	1.56	-5.51	0.00	0	0

frequency 100 KHz. and temperature 303K. The data are used to calculate the values of the related parameters listed earlier. The relevant data are presented in Table 1. The variation of dielectric constant (ϵ_0) with concentration of OHA in all the three non-polar solvents is displayed in Figure 1. The non-linear character of the curve is an indicator of the mutual interaction between the solute and solvent molecules, which may be better reflected from the g, ΔP and ΔG values evaluated in this study. Similar results have been reported by Garabadu and Swain [18] in their study on dielectric interaction in binary mixture.

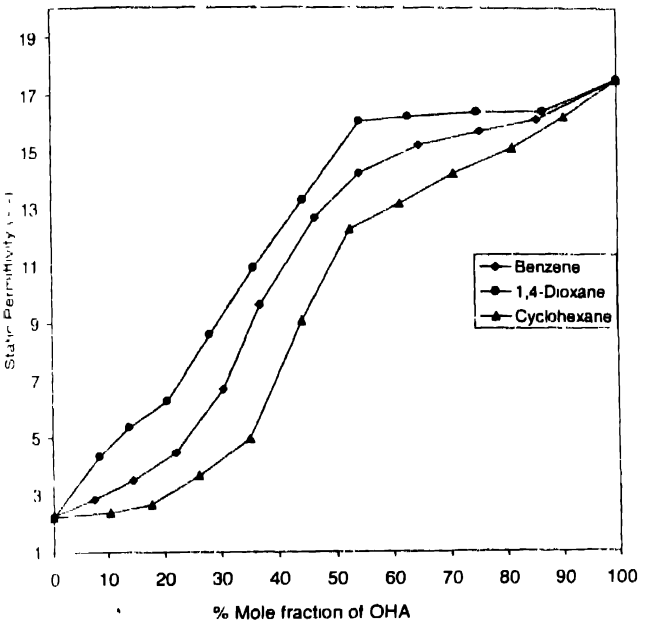

Figure 1. Variation of ϵ_0 with % mole fraction of OHA

The variation of g with the percentage mole fraction of OHA in three different non-polar solvents is plotted in Figure 2. The linear correlation factor (g) is a shape dependent parameter that helps in qualitative interpretation of the structure of the liquid under investigation. Its value is found to be unity in case of a normal liquid while it departs from unity for an abnormal liquid The value of $g > 1$ indicates predominance of α- clusters with parallel orientation whereas $g < 1$ reflects predominance of β-clusters with anti-parallel orientation.The change in the nature of multimerisation is associated with the change in the value of g and it is a concentration dependent phenomenon. It is clear from Figure 2 that below 0.2 mole fraction of OHA, g values are less than unity in benzene and cyclohexane. This suggests predominance of β- multimers in OHA deficient region. Above 0.2 mole fraction, the g value increase, attain a maximum value nearly at 0.5 mole fraction of OHA and then again start decreasing. On the other hand, binary mixture of OHA in 1,4-dioxane exhibits a different character where the value of g remains greater than unity throughout the concentration range. This may be attributed to the presence of intermolecular H-bonding of OHA with 1,4 -dioxane molecule.In all the three cases, the value of g is greater than unity in OHA rich region which reflects the presence of intramolecular H- bonding between hydrogen of -OH group and oxygen of acetyl group.It is also observed that the obtained g values are in the order 1,4-dioxane> benzene>cyclohexane. This may be due to the fact that cyclohexane and benzene are incapable of participating in hydrogen bonding with OHA. The higher g values of the binary mixture of OHA with 1,4-dioxane might be due the H- bonding of the hydrogen of either acetyl group or of hydroxy group of OHA molecule with the oxygen of the 1,4 - dioxane molecule. Also 1,4-dioxane is a more viscous solvent than cyclohexane and benzene and this in part accounts for the higher g values observed for OHA in 1,4-dioxane. Similar types of results were obtained by Antony and Smyth [19] for OHA and o-methoxyacetophenone in 1,4-dioxane and cyclohexane while observing the relaxation times.

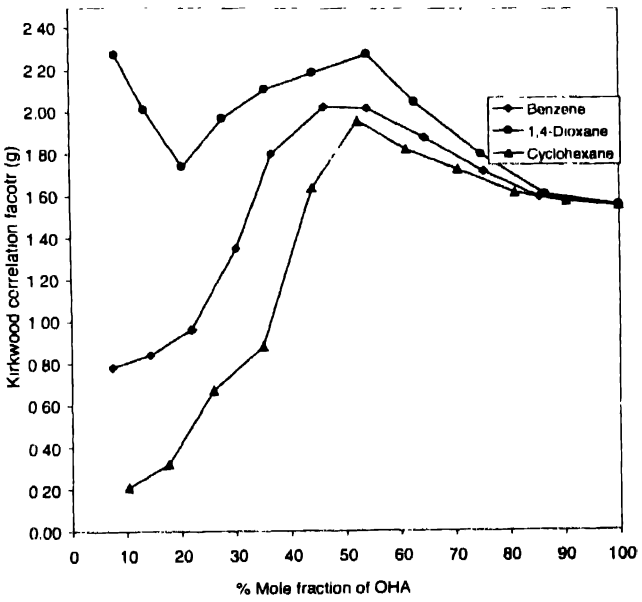

Figure 2. Variation of g with % mole fraction of OHA.

Figure 3 shows excess molar polarization DP (cc) of OHA with three non-polar solvents *viz.* benzene, 1,4-dioxane and cyclohexane plotted against percentage mole fraction of OHA at temperature 303K. The trend of variation in ΔP shows that it is positive over the entire concentration range of OHA in 1,4-dioxane environment for which $g>1$ throughout, while in cyclohexane it is partly negative. Predominance of β- clusters in the mixture of OHA and cyclohexane is the probable cause for negative value of ΔP, while greater conversion of β- to α-multimers is supported by positive ΔP due to reinforcement of angular correlation.

Davis and Douheret [16] developed a mixture equation purely from empirical consideration and introduced a parameter called excess correlation factor 'δg' to represent the departure from ideality. The term 'δg' in effect is identical to (g_{ab}-1) of the WQ equation[11]. The values of 'δg' are reported in Table 1.

Negative δg values indicate the lack of cooperative angular correlation. Table1 shows that in OHA-cyclohexane and OHA-benzene mixture that 'δg' value are negative in OHA deficient region. These negative values signify near complete destruction of angular correlation (β- clusters) between dissimilar molecule, while for OHA rich region and for the entire concentration range of OHA - dioxane mixture, δg values are positive indicating enhanced angular correlation (α- cluster).

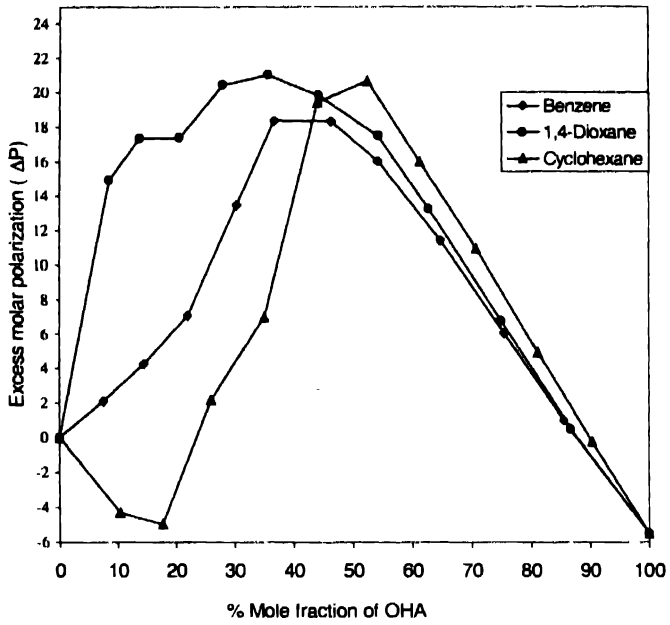

Figure 3. Variation of ΔP with % mole fraction of OHA

From Figure 4, the trend of variation of excess free energy (ΔG_{II}) shows that it is positive over the entire concentration range of OHA in all the three non polar solvents. With increase

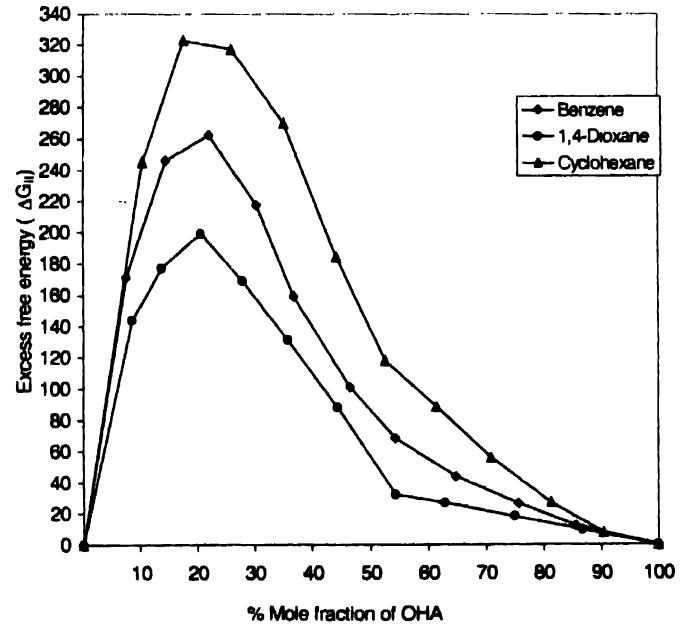

Figure 4. Variation of ΔG_{II} with % mole fraction of OHA.

in the concentration of OHA, ΔG_{II} increases, attains the maximum value in the range 0.17-0.22 mole fraction of OHA and than starts decreasing. This may be due to the fact that predominance of β - multimers in the mixture is characterised by reduction of internal energy. With further increase in the concentration of OHA, the conversion of β - multimers into α - multimers reverses the trend and ΔG_{II} starts decreasing. Similar result were obtained by us [9] for CHA. The magnitude of $(\Delta G_{II})_{max}$ for cyclohexane being highest corroborates our finding on g and ΔP that the extent of formation of β - clusters is maximum for this system. The values of ΔG_{II} decrease in the order cyclohexane > benzene > 1,4-dioxane. The minimum value in 1,4-dioxane supports our earlier finding that the solute solvent interaction in 1,4-dioxane medium is stronger than the other two media.

4. Conclusions

On the basis of above discussion, it may be concluded that

(i) α – multimers predominate throughout the concentration range of OHA in 1,4- dioxane due to intermolecular hydrogen bonding.

(ii) OHA deficient region in benzene and cyclohexane is associated with the predominance of β - multimers

(iii) In all the three solvents, the g - values greater than unity in OHA rich region reflects the presence of intramolecular H - bonding in OHA.

(iv) Excess free energy of mixing indicates the presence of strong solute - solvent interaction in 1,4 - dioxane as compared to cyclohexane and benzene.

Acknowledgments

The authors are thankful to the Head of the department of Physics & Principal, M.S.J. College, Bharatpur for providing laboratory facilities. One of them (K. K. Gupta) is indebted to the University Grants Commission for providing MRP to him and Manmath Sharma is thankful to the Council of Scientific & Industrial Research (CSIR) for providing JRF to him.

References

[1] A C Kumbharkhane, S M Puranik, C G Akode and S C Mehrotra *Indian J. Phys.* **74** 471 (2000)

[2] P J Singh and K S Sharma *Indian J. Pure Appl. Phys.* **34** 1 (1996)

[3] P J Singh and K S Sharma *Indian J. Pure Appl. Phys.* **34** 388 (1996)

[4] R Y Ghanbahadur, A C Kumbharkhane and S C Mehrotra *Indian J. Phys.* **68** 363(1994)

[5] R K Khanna and A Bhatnagar *J. Mol. Liquids* **38** 63 (1988)

[6] P F Mountain and S Walker *Adv. Mol. Relax. Process* **7** 105 (1975)

[7] K K Gupta, A K Bansal, P J Singh and K S Sharma *Indian J. Pure Appl. Phys.* **41** 57 (2003)

[8] S L Abd-El Messieh *J. Mol. Liquids* **105** 37 (2003)

[9] K K Gupta and P J Singh *Indian J. Phys.* **77B** 299 (2003)

[10] U S Mohapatra, G S Roy and S K Dash *J. Mol. Liquids* **106** 69 (2003)

[11] J Winkelmann and K Quitzsch *Z. Phys. Chem. Liepzig* **257** 45678 (1974)

[12] R H Cole *Ann. Rev. Phys. Chem.* **11** 149 (1961)

[13] C J F Böttcher *Theory of Electric Polarization* **Vol 1** (Amsterdam : Elsevier) p 261 (1973)

[14] S K Dash, V Chakravorty and B B Swain *Acta Chim. Hung.* **131** 799 (1994)

[15] B B Swain and G S Roy *Jpn. J. Appl. Phys.* **25** 209 (1986)

[16] M I Davis and G Douheret *Thermochim. Acta.* **104** 203 (1986)

[17] S K Raty and G S Roy *J Indian Inst. Sci.* **72** 487 (1992)

[18] K Garabadu and B B Swain *Indian J. Phys* **68** 271 (1994)

[19] A A Antony and C P Smyth *J. Am. Chem. Soc.* **86** 152 (1964)